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Problems Related to the Humification Processes in Soils of Temperate Climates

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I. INTRODUCTION

Soil organic matter (SOM) has been extensively examined because of its importance for soil fertility and productivity, and as a critical component in agricultural production systems [1]. Furthermore, its importance for establishing favorable physical conditions and architecture in soil has been emphasized. Because biological, chemical, and physical processes are involved in the balance between concurrent mineralization and immobilization of organic residues and nutrients, soils must always be considered in connection with their microflora and microfauna. The biochemical and enzymatic activity of the microbiota, as well as its buffering capacity, in regulating humification and the flow of nutrients, influence the processes related to the formation and transformation of SOM. It is, therefore, important to understand that soil humus is a dynamic system of both active and more passive components. These differ in biological availability, stability, and time of residence. Parton et al. [2] and Doran and Smith [3] suggested that short- and long-term changes in nutrient cycling and their response to organic management practices are associated with changes in the relative quantities of both the more labile and the more stable organic matter fractions. These relative quantities depend upon climate, soil type, and management. Furthermore, Janssen [4] indicated that differences in carbon and

nitrogen mineralization after 25 years of various management practices were more closely related to the amount of young soil organic matter than to the total C and N contents of a soil, indicating that qualitative changes are more important than gross quantitative changes. The latter changes, however, are also important. Scerbakow and Kislych [5] found a high correlation between the humus contents and the yields of agricultural plants in Chernozem soils. As the result of intensive management, these soils sometimes have considerable decreases in their C and N contents. Furthermore, a positive correlation between these contents and the activities of saccharase, protease, urease, and dehydrogenase were indicated. Beck [6,7] also observed a positive correlation among biomass, its enzymatic activities, and the humus content in soil samples from field plots under different forms of continuous management practices. By combining biomass and several enzymatic activities into an index, he predicted a long-term decrease in humus contents by specific management practices, if the index was smaller than that calculated from the actual organic carbon content. If this index was greater than that calculated from the actual humus content, a long-term increase in humus was predicted.

Investigations on the chemical structure of SOM fractions have also made considerable progress in the recent years. For instance, ^{13}C-nuclear magnetic resonance (NMR) spectroscopy has detected large differences in humic substances isolated from marine, aquatic, or terrestrial environments, including soils [8,9]. These differences usually involve the relative amounts of aliphatic and aromatic carbon contents. Such differences (e.g., in the structure of fulvic and humic acids from various soils) were not as obvious in previous degradative studies [10].

In soils, primary particles combine into aggregates of varying size. Tisdall and Oades [11] suggested that these aggregates are important factors in retarding soil organic matter decomposition. It was also shown that long-chain aliphatic or lipid compounds, together with polysaccharides, influence soil structure and the dynamics of nutrients [12,13]. Aggregates, therefore, are important factors for soil stability. Generally, the former view that humic compounds are stabilized mainly as the result of their complex and recalcitrant structure is only partly true. More important for stabilization are probably associations with metal ions and clays and aggregation [14,15]. Once this association is disturbed by climatic alterations or changes in soil management practices, the decay rates of SOM sometimes increase dramatically until a new equilibrium is reached. The last section of this chapter discusses these phenomena.

II. PLANT RESIDUES AS A SOURCE OF SOIL HUMUS

A. Whole-Plant Residue Materials and Their Transformation Rates

Plant residues introduced into soil are the main sources of humus. They consist of a wide range of different components, as shown in Table 1. On an average, they contain 15 to 60% cellulose, 10 to 30% hemicellulose, 5 to 30% lignin, and 2 to 15% protein. Additionally, they also contain minor amounts of phenols, sugars, and amino acids. During soil incubation of plant residues in a temperate climate, about 70% of the total residue carbon is released as CO_2 during the first year. The remainder decomposes more and more slowly with time and becomes steadily incorporated into soil humus. During the period of rapid decomposition, the morphological and chemical structures of the plant residues are drastically altered and the C:N ratio is narrowed by evolution of CO_2. Although complex processes are involved during the decomposition of the various ingredients, the overall degradation rate follows, reasonably well, first-order kinetics [16]. Residue decomposition in the field [17, 18] or in the laboratory [19] can be adequately described by

Table 1 Average Contents of Major Components in Plant Materials

	Percentage of Dry Weight			
Material	Cellulose	Hemi-cellulose	Lignin	Protein[a]
Ryegrass (mature)	19–26	16–23	4–6	12–20
Lucerne (stem)	13–33	8–11	6–16	15–18
Wheat straw	27–33	21–26	18–21	3
Pinus sylvestris (sawdust)	42–49	24–30	25–30	0.5–1
Beech wood	42–51	27–40	18–21	0.6–1

[a]Nitrogen × 6.25.
Source: Authors data and Ref. 36 and 36a.

assuming that plant materials consist of readily decomposable fractions that turn over in less than 1 year. Another, more stable, fraction has a turnover time of a few years. The decay of both the labile and the more stable fraction can be expressed as logarithmic functions, which can be combined to describe the overall process.

The composition of the organic residues incorporated into soil influences decomposition, as does temperature, soil moisture and texture, and other climatic and soil-derived characteristics. Kolenbrander [20] compared the decomposition of different organic residues under field conditions in the temperate climate. After the first year, 20% of green manure, 38% of straw, 60% of farmyard manure and 80 to 90% of peat remained as carbon residues in the soil. After 8 years, 3 to 10% of the plant residue and 20 and 50% of manure or peat carbon, respectively, were still present. Similar decomposition data were obtained in laboratory soil incubation experiments with different organic compounds and plant residues of increasing complexity, ranging from glucose, starch, and cellulose, to wheat straw, pine sawdust, almond shells, and cow manure [19]. As shown in Table 2, simple sugars or polysaccharides were readily utilized, and after 28 weeks, 90% of the glucose carbon and 85% that of the polysaccharides had been released as CO_2. With increasing complexity and lignin contents of the residues, degradation rates slowed. After 38 weeks of incubation, 32% of wheat straw carbon, about 50% of almond shell, and more than 65% of the ponderosa pine needle carbon remained in the soil.

The observation that the lignin contents of specific plant residues control degradation was presented by Herman et al. [21], who described the decomposition of root residue materials. This concept was further developed and used as a model to describe the decomposition rates of plant residues in soil by van Veen et al. [22] and Parton et al. [23]. The model developed by Parton et al. [23] is shown in Figure 1.

Plant residues consist of structural and metabolic materials that have, according to their lignin/N ratio, turnover times of 1 to 5 and 0.1 to 1 years. The metabolic C pool, defined by a low lignin/N ratio, is rapidly converted into a microbial C pool with a 0.1- to 1-year turnover time. Microbial and labile C together form the "active soil fraction," which consists of microbes and microbial products, with a short turnover time of 1.5 years. A larger pool of C and N forms a slowly transformable fraction that is physically protected and is in a chemical form that has more biological resistance to decomposition. The remainder of the active and the slowly transformable soil C is, with time, transformed into a fraction that is chemically recalcitrant and, additionally, is physically protected, and has the longest turnover time of 200 to 1500 years ("passive soil fraction"). It can also be assumed that the lignin/N ratio controls the division into structural and metabolic parts of the plant residues and that most of the lignin in residues flows into the slowly transformable soil pool. This direct flow of lignin is based on data from laboratory incubations of labeled lignin-type material by Stott et al. [24]. They showed that lignin is slowly catabolized to CO_2, but very little lignin C is found in microbial biomass, whereas 70% or more was being stabilized in the soil. Further variables in this model are annual precipitation, soil temperature and texture, the amount of annual plant residue input, and its lignin/N ratio. The model was used to predict future organic

Table 2 Decomposition of Various Organic Compounds and Plant Residues in Greenfield Sandy Loam Topsoil[a]

Substrate	Decomposition After Weeks[b]				
	1	4	12	20	28
Glucose	73	82	89	90	90
Starch	48	69	81	84	86
Cellulose	27	52	77	79	84
Green matter (corn 28 days)	27	45	69	73	82
Lima bean straw	36	57	75	78	79
Wheat straw	20	33	59	61	64
Corn straw	18	31	60	63	65
Cow farmyard manure	18	33	43	48	50
Prune wood (sawdust)	12	25	33	40	45
Almond shells	12	24	37	39	41
Douglas fir (sawdust)	2	5	15	29	34
Peat moss	<1	3	8	14	17
Soil humic acid	<1	<1	1	1	2

[a]Dry, powdered (1-mm) material was mixed (1000 ppm) with soil and incubated at the -33 kPa water potential at 22°C in the laboratory under continuous aeration.
[b]Percentage of added carbon evolved as CO_2.
Source: Data from author and Ref. 19.

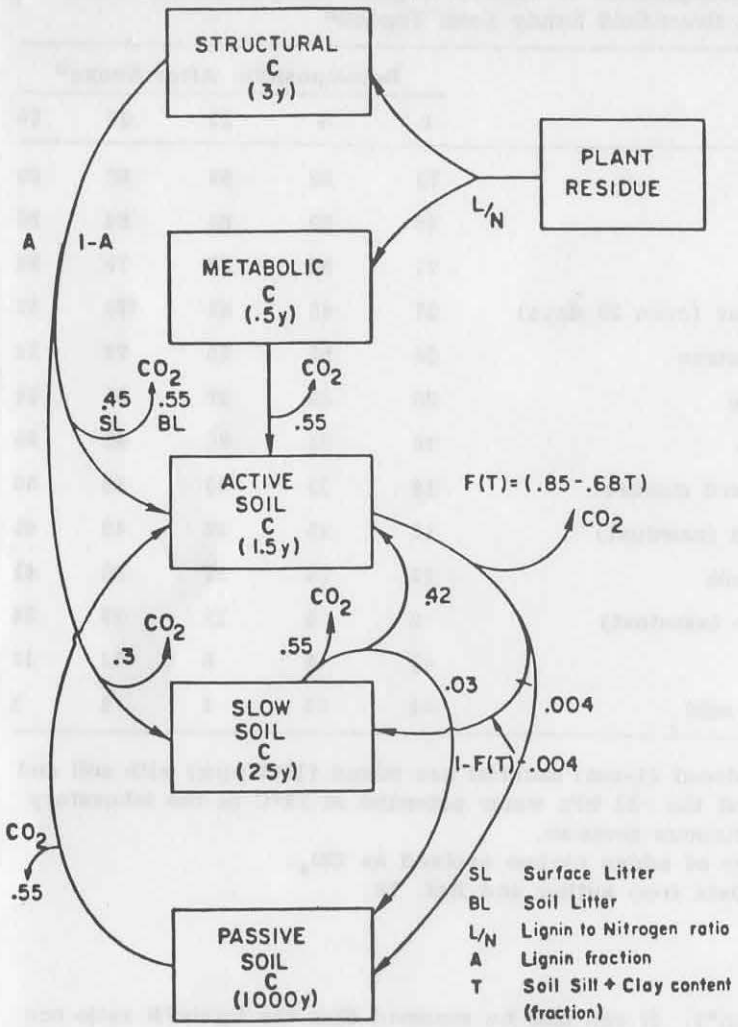

Figure 1 Diagram of the carbon flows through a readily available fraction (active soil C), a physically or chemically protected fraction (slow soil C), and a chemically recalcitrant and physically protected fraction (passive soil C). Ciphers indicate carbon mineralization rates [23].

matter levels and the carbon and nitrogen flows in the Great Plains area of the United States.

Several authors [2,25,26] have emphasized the importance of young and easily decomposable humus in determining the flow of carbon and nutrients. Although there is an exchange of organic C from the passive into the active phase and vice versa, it is necessary that the active phase be continuously supplied with fresh organic material, which also sustains a vigorous microbial population [4].

B. Degradation and Transformation of the Main Plant Components: Cellulose and Lignins—Metabolism and Cometabolism

Cellulose and Hemicelluloses

Earlier studies [27,28] indicated that cellulose and hemicellulose components of plant residues are more rapidly decomposed than the lignin component. The ^{14}C-labeling of these components has considerably aided investigations of their decomposition rates and of the fate of the remaining carbon [24,29–31].

Cellulose loses about 75% of its carbon during the initial 4 months of soil incubation; after 1 and 2 years, only 18 and 16% of the initial carbon, respectively, was left in the soil (Table 3). About 20% of the residual carbon after 1 year of incubation was found in the microbial biomass. A greater portion (60 to 80%) was present in 6 N HCl hydrolyzable portion of the soil and, here, mostly in microbial metabolites, such as amino acids and sugars [31,32]. Sörensen [33] reported, based on field incubation experiments in which ^{14}C-labeled wheat straw was incubated for 20 years, that during the 8- to 20-year period, the proportion of residual ^{14}C in biomass or in amino acids from the hydrolyzable portion was nearly constant and averaged 3 to 22% of the remaining ^{14}C in soil.

Cellulose and hemicelluloses can be completely metabolized by numerous soil microorganisms and used as a sole carbon source for growth. These organisms include bacteria, actinomycetes, and fungi. The pathways and enzymes involved in the degradation of these polysaccharides are well characterized for several bacteria [34–36] and seem to be similar for most of the cellulolytic organisms. The degradation of crystal cellulose involves a random attack on the polysaccharide chain by *endo*-1,4-β-glucanases and the production of smaller units, which are afterwards cleaved from the free ends by *exo*-1,4-β-glucanases and glucosidases into cellobiose and glucose. The metabolic products can then be completely used by microbes for the production of energy and biomass.

Hemicelluloses are generally considered to be degraded faster than cellulose [37,38], probably as the result of a greater number of microorganisms that can use these compounds as a substrate.

Table 3 Biodegradation and Incorporation into Biomass and 6 N HCl Hydrolyzable Portions After Incubation of Soils (Typic Hapludalf and Mollic Haploxeralf) for Different Periods with Various ^{14}C-labeled Organic Compounds

	% ^{14}C-CO_2 evolved				% ^{14}C in biomass		% ^{14}C hydrolyzed[a]	
	Months							
Compound	1	6	12	24	12	24	12	24
Glucose (UL ^{14}C)[b]	70	85	89		19		72	
Wheat straw polysaccharide (UL ^{14}C)[b]	55	78	81	84	10	8	60	58
Wheat straw (UL ^{14}C)[b]	31	63	69	71	7	5	56	48
Lignin[c] ^{14}C-ring	5	26	33	45	0.5	0.4	19	18
Lignin[c] ^{14}C-side chain	7	28	34	42	0.5	0.4	21	19

[a]Percentage of residual ^{14}C in soil.
[b]Uniformly ^{14}C-labeled.
[c]Cornstalk material with ^{14}C label in the lignin portion at aromatic rings or at C-β of the side chains, respectively [30].
Source: Refs. 19,24,31.

Cheshire [39], however, observed that ^{14}C-labeled hemicelluloses are decomposed similarly to cellulose, but that parts of their sugars are recycled into other sugars of microbial polysaccharides. Furthermore, soil polysaccharides also can partially be directly derived from plants [39].

Lignin

The biodegradation of lignin is less well understood than that of cellulose. This is partly the result of the complicated structure of lignin, in which phenylpropanoid units—the lignin alcohols—are connected irregularly by C-O-C and C-C linkages. Lignin consists of

large spheric molecules with a mean relative molecular mass (M_r) between 10,000 and 20,000 daltons (d). In the plant cell wall, lignin is additionally linked to hemicellulosic and, possibly, to cellulosic components [36]. The complex aromatic structure is only slowly attacked by microbes and, as it turns out [40], this attack is not directed toward a distinct type of linkage as in cellulose. Fewer species of microorganisms can degrade lignins than can degrade cellulose. The most active biodegraders of lignin belong to the white-rot fungi. These, however, are not common in arable soils, but can be found in forest soils. Lignin degradation and transformation in arable soils seem to be mostly a domain of the Fungi Imperfecti, the actinomycetes, and other bacteria [15,41]. The bacteria (including actinomycetes) exhibit only a limited activity in degrading high-molecular-mass lignin or the lignin portion of lignocelluloses. In arable soils, lignocelluloses are probably degraded by synergistic consortia of microbes that cannot completely use them individually.

Several observations highlight the peculiarities of the biodegradation of lignin, compared with that of cellulose or other polysaccharides: None of the organisms yet isolated can use lignin as a sole carbon source. An additional easily available carbon and energy source is always needed for degradation and, therefore, it is a *cometabolic* degradation. For this kind of degradation, Kirk and Farrell [40] coined the expression "enzymatic combustion," because no energy or metabolites can be gained from lignin for growth purposes of the ligninolytic organisms. Furthermore, degradation of lignin is much more vigorous under aerobic than under anaerobic conditions [42,43]. Colberg and Young [44] have reported that only lignin precursors with an M_r between 600 and 1200 d are degraded by mixed or pure cultures of anaerobic bacteria. This occurs by anaerobic cleavage of arylether linkages and conversion of the resulting phenols into CO_2 and CH_4. Higher molecular mass lignin was not converted at all.

Incubation of soil samples with ^{14}C-labeled lignin or lignocelluloses [24] indicated that during a 1-year period, about 15 to 30% of the lignin carbons were released as CO_2. Very little (< 1%) of the residual carbon was incorporated into the biomass, and on 6 N HCl hydrolysis of the soil, most of it remained in the nonhydrolyzable fraction (see Table 3). This is explained by the fact that microorganisms cannot use lignin as a carbon and energy source during degradation. Furthermore, lignin is vigorously catabolized only in well-aerated soils, whereas in poorly aerated soils or anoxic sediments and swamps, lignin degradation is very slow or not measurable [42]. This recalcitrance of lignin under anaerobic conditions is considered a major factor in the accumulation of peats, and most probably, of coal.

Information is now available about the biochemical pathways of lignin biodegradation and the specific enzymes involved. Characterization of a microbially attacked lignin by ^{13}C-NMR spectroscopy [45–47] or by mass spectrometry [48] showed a cleavage of bonds in both side chains and rings. This results in partly alphatic–aromatic degradation products, which, however, are still linked into a macromolecular matrix. Only at later stages of degradation are numerous monomer or dimer degradation products released, which originate from lignin by an extensive cleavage of side-chain and ring linkages [40]. Several of these products are shown in Figure 2. Furthermore, there is a considerable increase in polar groups, including keto, hydroxyl, and carboxyl groups.

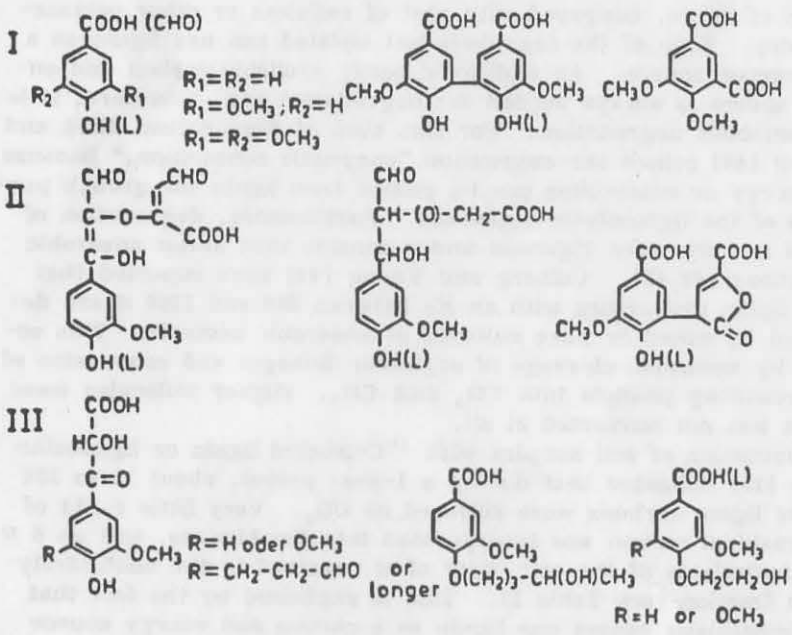

Figure 2 Degradation products detected in white rot-infected spruce or beech wood lignin, sometimes in connection with larger lignin residues (L). I. Derivatives of benzoic acid, benzaldehyde, or phthalic acid originating through cleavage reactions in lignin side chains; II. Derivatives originating through cleavage reactions of neighboring rings; III. Derivatives substituted by parts of the side chains from neighboring subunits. Adopted from [40,45,46,48].

Extracellular enzymes have been isolated from the culture fluids of ligninolytic fungi, mainly from those of *Phanerochaete chrysosporium* that vigorously catalyze the degradation of dimeric and trimeric lignin models [49]. The enzymes function similar to H_2O_2-dependent peroxidases, but they have the specific capability to remove electrons from aromatic rings with completely etherified hydroxyl groups. This yields cationic radicals that stabilize by cleavage of C_α-C_β bonds and the formation of further radicals (Fig. 3; according to Schoemaker et al. [50]). The intermediate radicals can react with O_2 or water and become stabilized by the formation of hydroxy or keto derivatives. The enzymes also catalyze additional cleavage reactions, including bonds connecting C_α from the side chain to the ring or of bonds in the aromatic rings [51,52]. These reactions can occur with lignin models before they are degraded into smaller units.

The enzymes isolated from ligninolytic fungi catalyze only the degradation of low-molecular-mass lignin models, but have very little effect on the lignin itself [51,53]. Kirk [51] theorized that ligninolytic fungi that completely degrade lignin have additional enzymes or cofactors residing on cell surfaces. More probably, however, seems to be a transient binding of lignin on cell surfaces combined with the release of more water-soluble lignin products [54]. This binding is probably a prerequisite for lignin degradation, as it enables the enzymes involved to function cooperatively.

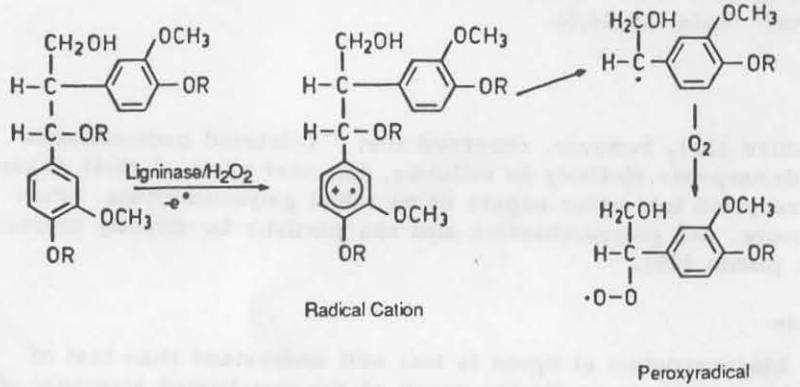

Figure 3 Action of the ligninase–H_2O_2 complex on lignin models: R, connection to lignin subunits or ethyl methyl substituents. (According to Ref. 50.)

The concept of a nonspecific enzyme-catalyzed radical mechanism provides, however, a better way in understanding the peculiarities of lignin degradation and its transformation into humus. It indicates that radical formation results in a random opening of the bond system, in an addition of nucleophilic groups and, in this connection, in the formation of more polar groups. In soils, these still high-molecular-mass fragments, containing additional functional groups and radicals, can react with humic compounds already present, with metal cations, or with clay surfaces saturated with transition metal ions [55]. By this mechanism of degradation, the lignin polymer undergoes gradual slow modifications during incorporation into humus. The earlier concept that lignin is first degraded into phenols, which then are either microbially metabolized or repolymerized into humus [14,15,56], is likely to be revised. It appears more probable that partly degraded lignin or lignin fragments become adsorbed or bonded by the already present organic and inorganic matrix.

C. Transformation of Phenolic Compounds

As the macromolecular lignin matrix is attacked only randomly, lignin-derived phenols are released in only small amounts during progressive stages of degradation. Phenols and phenolic acids, however, have been identified in soil extracts from many different soil systems [57,58]. They are derived from decomposing plant residues, microbial biosynthesis, or root exudation. Phenols have been implicated in various soil processes, including abiotic humus formation [59], dissolution of minerals [60], or as possible phytotoxic or allelopathic chemicals in field situations or hydroponic cultures [61, 62].

Indigenous soil microbial population have no difficulty degrading or transforming exogenously applied phenols or phenolic acids. This includes the splitting of aromatic rings and their metabolization into microbial biomass [63,64]. However, in many soil systems, microbial or physicochemical reactions with soil or humus particles may reduce the concentration of phenols in the free form and result in their adsorption by the bulk soil material. Low concentrations of ferulic acid, catechol, and catechol derivatives were more readily adsorbed and linked into soil humus, whereas higher concentrations were more readily microbially degraded [65]. Lehmann et al. [66] noted that phenolic acids (ferulic, caffeic, protocatechuic, or *p*-hydroxybenzoic acids) were oxidized in soil by Fe^{3+} or Mn^{4+}. They concluded that the reactions of phenols were predominantly chemical and were oxidatively coupled with soil humus upon reduction of Fe^{3+}- and Mn^{4+}-oxides. The activity of microbes associated with the sorption of phenolic acids in soil is also likely [65,67]. A stimulation of the

microbial decomposition of certain aromatic and phenolic aldehydes in soil with added montmorillonite was also observed by Kunc and Stotzky [67a] and reviewed in more detail by Stotzky [67b]. In view of this rapid disappearance of certain phenolic acids in various soil types, it is obvious that, under field conditions, the free form of these compounds may not persist for long periods. Only in the vicinity of decaying plant residues or at root surfaces can they be present in appreciable concentrations. Diffusion into the soil environment rapidly reduces their dissolutive or allelopathic potentials.

The chemical structure of phenolic compounds greatly influences their sorption or degradation in soil. Several authors [63,66–68] observed increasing adsorption from *p*-hydroxybenzoic < vanillic < *p*-hydroxycoumaric < ferulic < protocatechuic < caffeic acids; but decreasing degradation rates. This suggests that sorption and degradation of the compounds is affected by their functional groups and, most probably, by their respective ease of being oxidized into semiquinones or quinones. Cheng et al. [69] observed that 80% of [^{14}C]catechol applied at 1 $\mu g\ g^{-1}$ soil was bound in a neutral soil after 80 days of incubation, whereas about 75% of ^{14}C–ring-labeled vanillic acid was decomposed to $^{14}CO_2$ during the same time [63]. Dalton et al. [67] discussed that the acrylic side chain (e.g., in ferulic, *p*-coumaric, or caffeic acids) could also account for the enhanced binding, as the α,β unsaturated bond in the side chain is more susceptible to electrophilic addition or to reactivity with polyvalent metal cations.

In a previous chapter in this series by Haider et al. [70], the microbial formation of phenols and quinones and their contribution to humus synthesis were described and, therefore, will not be addressed here.

D. Degradation and Transformation of Nitrogen-Containing Compounds

Proteins, amino acids, amino sugars, and nucleic acids, either in plant residues or in dead microbial cells, are generally readily degraded or transformed in soil. Natural grasslands and forest ecosystems normally develop a dynamic equilibrium between organic N inputs to the soil and mineral N uptake by roots. Agroecosystems, on the other hand, have developed from mixed- and multiple-cropping systems to intensively managed monocultures with large and pulsed N inputs in the form of commercial fertilizer. In these latter systems, the return of organic C and N in the form of plant residues is small, compared with the total input of N.

The turnover of nitrogen in soils is closely related to heterotrophic metabolism, energy generation, and its utilization for biosynthesis

[71,72]. Empirical research has demonstrated that decomposition of agricultural or other plant residues, in general, is influenced by their C:N ratio [73]. If the plant C:N ratio is greater than 25:1, N will be taken up from the mineral N pool or from simultaneously attacked soil organic matter, as the developing heterotrophic microbiota has a C:N ratio of about 10:1. Observations by Allison and Killham [74], however, suggest that with repeated application of straw to arable soils, the degradation becomes progressively more rapid. This may be because of a marked increase in the activity of fungal biomass that has a wider C:N ratio than the bacterial biomass or has the ability to attack lignin. Fungi may then be able to derive nitrogen that is associated with lignocelluloses; this was described for forest soils during the decomposition of tree litters, with a C:N ratio of about 50:1 and, also, for the decomposition of straw that was low in available N content [74,75].

The soil microflora is the prime decomposer of organic substrates and, therefore, is an important mediator in the metabolic turnover of C and N. Similar to the turnover of C, the heterogeneous availability of N in organic materials can be observed. Van Veen and Frissel [76] developed a mineralization–immobilization submodel for N and C. This model differentiated between N-containing readily decomposable materials, N in resistant active materials and lignin, and N in old organic matter. Similar to the model for carbon flow (see Fig. 1), a model for the N flow was presented by Parton et al. [23] that distinguishes between structural and metabolic N in plant residues and flows into an active, a slow, and a passive soil N pool. The value of defining and measuring soil organic fractions in the characterization of the quality and activity of organic matter was also demonstrated by Janssen [4]. By using a model to separate the decomposition rates of "young" and "old" SOM, he illustrated the effect of long-term amendments with mineral N, green manure, and animal manure on mineralizable soil N. This soil N fraction was more closely related to the amounts of young organic matter than to the total N contents of the soil. The young organic matter was defined here as the fraction that accumulated by addition of crop residues or farmyard manure during 25 years of various management practices.

As is now also becoming apparent, the soil fauna [77,78] and the plant rhizosphere [79] have an important role in N cycling. It is, however, difficult to quantify these effects, because in addition to their direct contribution to N fluxes, there is a wide range of indirect effects on the soil as an environment for microorganisms and plant roots.

III. NEWER CONCEPTS ABOUT THE STRUCTURE AND CHEMICAL COMPOSITION OF SOIL ORGANIC MATTER

Two approaches to the elucidation of humic structure are commonly utilized. These are the so-called degradative and nondegradative approaches. In the first approach, humic substances are chemically or physically broken down into various "subunits" that are subsequently isolated and identified. In the nondegradative approach, isolated humic substances are analyzed directly, utilizing techniques that allow structural inferences to be made. Nuclear magnetic resonance spectroscopy (NMR) is central to this approach.

It is beyond the scope of this chapter to discuss the chemical structure of humus and its fractions in detail, and it is described only to the extent that is directly related to humification and to soil functions. More detailed information can be found in books edited by Christman and Gjessing [80], Aiken et al. [81], Frimmel and Christman [82], and Hayes et al. [82a]. Details on degradative methods for studying humic compounds, particularly by permanganate oxidation, were published by Schnitzer [83]. The application of pyrolysis–mass spectrometry, including gas chromatography–mass spectrometry (GC-MS) analysis of the fragments, was recently reviewed by Schulten [84]. A review on the application of NMR techniques to soil chemistry was published by Wilson [85].

Integration of ^{13}C-NMR spectral areas can be used to estimate the relative concentrations of the various carbon signals. Usually, liquid or solid-state cross-polarization–magic-angle spinning (CP-MAS) ^{13}C-NMR spectra ranging from 5 to 200 ppm are divided into four ranges of chemical shifts: 5 to 46 ppm, designates the aliphatic region; 46 to 110 ppm, the C-O/C-N region; 110 to 160 ppm, the aromatic or olefinic region; and 160 to 200 ppm, the carboxylic or carbonyl region. Typical spectra of humic compounds and the average composition determined by integration of solution or CP-MAS spectra from humic acids from different soils are shown in Figure 4 and Table 4 [86].

Schnitzer and Preston [87] show that the relative intensities of areas, even from a set of similar humic materials, should be regarded as estimates and interpreted with caution. Moreover, Norwood [9] criticized that only few workers bother to ensure that their NMR acquisition parameters have been optimized for quantitative analysis. Fründ and Lüdemann [86] made an extensive comparative study of representative humic materials from Bavarian and northern German soils, to learn how much quantitative structural

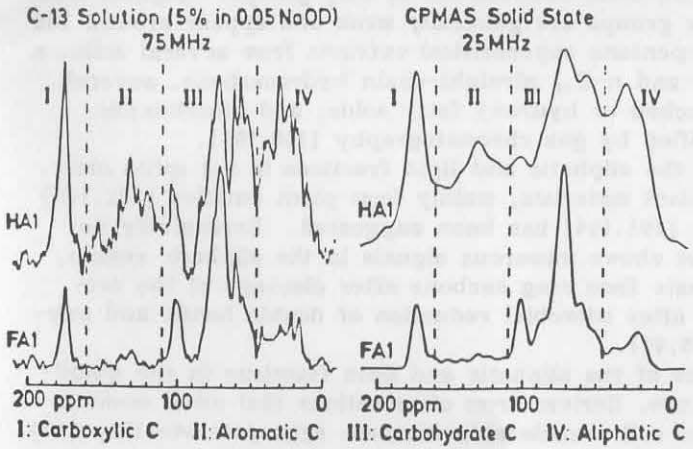

Figure 4 Comparison of the solution (NAOD, deuterated sodium hydroxide) and CP–MAS (cross-polarization–magic-angle spinning) ^{13}C-NMR spectra of humic and fulvic acid fractions from a Mollisol Randoll [86].

information could be gathered from ^{13}C-NMR studies by optimizing NMR parameters. In general, solution and CP-MAS spectra of the humic materials agreed within ±2% of the distinct spectral areas. However, the data obtained for soluble humic fractions from highly aromatic soils made it obvious that, by CP-MAS spectra, the aromatic region was grossly underrepresented.

A. Aromaticity of Humic Compounds

At the low field of ^{13}C-NMR spectra, signals of aromatic rings, 115 to 130 ppm, indicate highly protonated rings. Resonances between 130 and 147 ppm suggest substitution of the aromatic rings by carbon functions [87]. Distinct peaks between 150 and 160 ppm appear to arise mainly from phenolic C- or from N-substituted aromatics. In humic acids the latter signals are usually rather small. Humic acids from highly oxidized soils show the lowest level of phenolic carbons, whereas humic acids from peats are higher in phenolic and methoxyl (58 to 60 ppm) carbons. Therefore, ^{13}C-NMR spectra of soil humic acids and, even more, of fulvic acids, show less polyphenolic character than formerly thought [8,9]. This theory of a significant contribution of phenols and other aromatic compounds to both humic and fulvic acids is based mainly on the former

Table 4 Average Composition of Humic Materials from Different Soils Determined by Quantification of ^{13}C-NMR Spectra in NaOD Solution[a] or of CP-MAS[b] Spectra

	Carboxyl-C (205–160 ppm) (%)	Aromatic-C (160–110 ppm) (%)	C-O/C-N-C (110–46 ppm) (%)	Aliphatic-C (46–5 ppm) (%)
Solution spectra[c] (75 MHz)	14.3%	14.4%	47.3%	23.8%
CP-MAS spectra[c] (75 MHz)	14.8%	11.3%	49.0%	24.9%
Solution spectra[d] (75 MHz)	12.0%	17.7%	49.0%	21.3%
CP-MAS spectra[d] (75 MHz)	12.5%	13.6%	51.9%	22.0%

[a]Deuterated sodium hydroxide.
[b]Cross-polarization–magic-angle spinning.
[c]From nine German soils (south and north Germany).
[d]From 20 German and Spanish soils.
Source: Data from Ref. 86.

theory of a close structural relationship between humic compounds and lignin. Furthermore, earlier degradative studies with permanganate indicated that humic and fulvic acids consist mainly of aromatic nuclei and highly substituted aromatics, with either cross-linking aliphatic side chains or functional groups, such as carboxyl, hydroxyl, or methoxyl [10,83]. From ^{13}C-NMR spectra of humic acids from Typic Borolls in Saskatchewan, Canada, Schnitzer and Preston [87] reported that the aromatic region contributed between 35 and 45% to the total carbon distribution. Fulvic acids from aerobic soils show many structural similarities to humic acids, but with a higher level of carboxyl and C-O groups and with a lower aromatic content [8,88].

The polyphenolic structure of lignin undergoes substantial modifications during degradation and humification, which include side chain and ring cleavage reactions (see under Sect. II.B). Almendros et al. [89] showed by ^{13}C-NMR spectroscopy of whole compost or humic acid extracts during a continuous aerobic composting process of straw and grape husks, that typical lignin structures

completely disappeared or decreased strongly after 4 months, whereas aromatic signals in the range from 100 to 130 ppm became more prominent. There was also a large increase of signals in the aliphatic region.

If, however, woody plant tissues are degraded anaerobically, as in anoxic sediments, swamps, or during peat formation, materials directly related to lignin structures become relatively enriched and appear in ^{13}C-NMR spectra as the result of a more rapid degradation of polysaccharides [90]. Fragments obtained by pyrolysis [91] or fragments obtained by CuO oxidation of humic acid extracts from buried woods or peat [92] confirmed the presence of typical lignin-like materials. This indicates that the alterations of lignin during decomposition under anaerobic or O_2-limiting conditions are less complete than in well-aerated soils.

After CuO oxidation, most of the phenylpropanoid units of lignin in lignocelluloses appear in the form of aldehydes and very little as acids. Fresh vascular plant tissues, after this oxidation, yield ratios of vanillic acid/vanillin and syringic acid/syringaldehyde in the range of 0.1 to 0.2. The acid/aldehyde ratios are significantly elevated after CuO oxidation of microbially altered sedimentary plant fragments [93] and in the profile of mull or moder raw humus (Mollisols) of forest soils with increased depth [94,95]. In humic or fulvic acids from arable soils, acid/aldehyde ratios, if they can be measured at all, are generally very high [92]. These consistent patterns of increased acid/aldehyde ratios correspond to decreased lignin and aromatic methoxyl contents and are characteristic of the progressive microbial decay of lignin [92,94,95].

B. Aliphatic Derivatives in Humic Compounds

The ^{13}C-NMR spectra of humic compounds generally exhibit strong signals between 17 and 33 ppm, which probably indicate CH_2 groups in long paraffinic chains or in alicyclic or heterocyclic saturated ring structures. This assumption is based on the low intensity of signals in the region where CH_3 groups (around 16 ppm) are to be expected [86,87]. By integration, the aliphatic region represents from 16 to 20% or more of the entire carbon content (see Table 3). In addition to the aliphatic carbon content of humic compounds, a lipid fraction can be extracted from soils by simple Soxhlet extraction with organic solvents [96]. These lipidic compounds are accumulated in acidic soils, where they can represent up to 30% of the total organic matter. By extraction with supercritical nonpolar solvents, the aliphatic fraction can be obtained in even higher yields [13,97–99].

Most of the ^{13}C-NMR signals of the extracted aliphatics and lipids appear in the zero to 40 ppm region and are mostly the result

of CH_2 groups with little contribution of CH_3 groups. Signals from carboxyl or ester groups are generally weak and appear around 180 ppm [99]. In *n*-pentane supercritical extracts from several soils, a number of *n*-C_{24} and *n*-C_{26} straight-chain hydrocarbons, several unsaturated branched or hydroxy fatty acids, and dicarboxylic acids were identified by gas chromatography [100,101].

The origin of the aliphatic and lipid fractions is not quite clear. An origin from plant materials, mainly from plant cuticles [102,103] or from microbes [101,104] has been suggested. Extensively degraded lignin also shows numerous signals in the aliphatic region, which may originate from ring carbons after cleavage of the aromatic nuclei and after microbial reduction of double bonds and oxygen functions [46,47].

The importance of the aliphatic and lipid fractions in the stability of soil structure, derives from observations that small amounts of lipids added to soil considerably increase aggregate stability [12]. It has been suggested that the lipidic substances form water-repellant films of oriented molecules on the surface of aggregates. Capriel et al. [13] showed a positive correlation between the quantity of an aliphatic fraction extracted from soils by supercritical *n*-pentane and the aggregate stability.

C. Fulvic Acids and Dissolved Organic Carbon in Soil

Another prominent region in the ^{13}C-NMR spectra of humic compounds from 46 to 110 ppm represents carbons linked with singly bonded O or N. This region is sometimes called the "carbohydrate-derived region," as it is suspected that in most humic materials, polysaccharides are the major parent compounds for these carbons. However, ether and amino derivatives also have shifts in this region.

Polysaccharides themselves can be separated from soil or soil organic matter by several extraction techniques [105,106]. The polysaccharides consist of relatively well-defined sugar units that can be isolated after hydrolysis [39]. By ^{13}C-NMR spectroscopy, the signals can be assigned mostly to sugar units by chemical shift tables [107].

This 46 to 110 ppm area is less well-defined in humic and fulvic acids. As the result of the broad peaks, an assignment to known sugar signals is difficult. Furthermore, aliphatic ethers, which also absorb in this region, could be of importance as structural units in humic compounds [108]. In fulvic acids, however, some better-defined signals at 105 ppm can be assigned to the anomeric C-1 of sugars. Hatcher et al. [8], as well as Preston and Ripmester [109], pointed out that polysaccharide-derived structures contribute substantially to fulvic acids. Saiz-Jimenez and de Leeuw

[110] also concluded this from results obtained by pyrolysis–gas chromatography of fulvic acids from Typic Xerochrept and podzol soils. They claimed that the fulvic acids consist mainly of polysaccharide units or remains of polysaccharides, in addition to varying contributions from lignin and fatty acids. Care must be exercised, however, in interpreting evidence of a more-or-less polysaccharide-derived nature of fulvic acids, unless precautions have been taken to separate associated from unassociated polysaccharides [111].

As the result of a higher content of functional groups, fulvic acids have a higher cation-exchange capacity than humic acids. The well-known and frequently described function of fulvic acids in forming water-soluble and water-insoluble metal complexes and their activity in the weathering of minerals will not be discussed here. The reader is referred to reviews by Schnitzer [112] as well as by Stevenson and Fitch [113], which deal particularly with these topics. More important in the context of this chapter is the role of soil fulvic acids in the formation of most of the dissolved organic matter (DOC) in soil and ground waters and probably also in streams and lakes. In surface waters, unique humification processes, including those of falling leaves, also may be of importance [114,115].

The DOC can act as a carrier of trace metals, and in surface waters, it also can bind organic chemicals, including pesticide residues or other pollutants. Gauthier et al. [116] provided evidence that extremely hydrophobic pollutants (e.g., polycyclic hydrocarbons, DDT, mirex) have a strong tendency to associate with organic matter in water. Zepp [117] indicated that this association results in a large enhancement in the rate of light-induced dechlorination and degradation of such persistent pollutants. The mechanism of this enhanced light-induced degradation of pollutants bound to DOC is unclear. It is possible that superoxide, organoperoxyl radicals, or singlet oxygen, in concert with the direct photoreactions of humic substances, may be involved [117; and literature cited therein].

The DOC also has an important role in the formation of chlorinated organic compounds, which are sometimes toxic, as a result of the chlorination of water for drinking purposes [118]. Some of the chlorinated by-products are weakly mutagenic. However, a chlorofuranone (Fig. 5) and several similar compounds with highly mutagenic potentials have been isolated and identified. They occur in pulp effluents as by-products after chlorine bleaching or after chlorination of DOC-containing waters for drinking purposes [118].

Concentrations of DOC in groundwaters or aquifers are generally small and range from about 0.5 to 0.7 mg carbon per liter [119]. Sometimes, however, acquifers that receive recharges from peat or

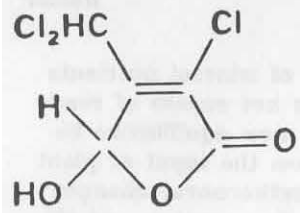

Figure 5 3-Chloro-4(dichloromethyl)5-hydroxy-2(5*H*)-furanone, one of the mutagenic chlorofuranones identified in chlorinated pulp effluents or in chlorinated humic substances [118].

swamps are higher in groundwater DOC. Similar to soil fulvic acids, ^{13}C-NMR spectra indicate that DOC in groundwater contains little aromatic C, but is rich in aliphatic C, including C-O functions and carboxyl groups [114,119]. Only 1 to 4% of the organic carbon, however, can be accounted for by carbohydrate components. Apparently, humic substances present as DOC in groundwaters have lost their carbohydrate contents through microbial decay, probably as the result of their long residence times in groundwaters [119]. Only DOC from upper soil layers seem to contain more typical polysaccharides, as indicated by Guggenberger [120] for DOC from mull horizons of forest soils.

The microbial availability of DOC is important for its use as a carbon source for denitrifying organisms. Inasmuch as the nitrate content of groundwaters appears to be increasing because of the increasing use of N fertilizers, the question is whether DOC in groundwaters helps to diminish nitrate contents. Sometimes the denitrifying potential of DOC is calculated as if its carbon contents were equal to those of glucose and other readily available carbon sources and could be used completely by heterotrophic denitrifiers [121]. Given the limited knowledge about the structure of DOC, precaution is urged in assuming that DOC is an easily available carbon source, particularly at greater depths in the unsaturated and saturated zones of water catchment areas.

IV. IMPACT OF THE ENVIRONMENT ON HUMUS FORMATION AND DEGRADATION

A decline in soil organic matter levels generally occurs when virgin soils under natural grasslands or forests are cleared and brought into agricultural production. This net mineralization of soil organic

matter is accompanied by an enhanced release of mineral nutrients that are utilizable for plant growth. Once the net excess of readily decomposable organic matter is depleted, a new equilibrium becomes established between humus synthesis from the input of plant residues and humus decompositon [3,122]. Furthermore, changes in agricultural management, including changes in cropping and tillage, fertilizer, or water management and climatic changes, influence soil organic matter levels. These changes impinge on the crop productivity of soils, erosion potential of soils, and the storage and turnover of nutrients in soil [3,123].

A. Aggregation

As already described in the preceding sections, microbes decompose plant residues, and the resulting microbial products become substrates for humus formation. Polymerization and adsorption result in compounds with relatively high molecular mass that are susceptible to various types of chemical and physical bonding with clays and amorphous mineral colloids [67b].

Organic amendments have favorable effects on physical properties and improve soil structure. The aggregation of microaggregates into macroaggregates is typical for well-structured soils that have a greater resistance to erosion and improved air–water relations [124, 125]. Tisdall and Oades [11] suggested that microaggregates are combined into macroaggregates by transient (i.e., easily decomposed) microbial- or plant-derived polysaccharides and by roots and hyphae. Easily degradable lipids also seem to be of importance [12,13]. More persistent binding agents are responsible for the integrity of microaggregates and consist of humic materials in association with amorphous Fe and Al compounds and polyvalent metal cations [11,125].

The reduction of humus levels, as the result of cultivation, causes a decrease in macroaggregates and an increase of microaggregates. Elliot [126] indicated that the organic matter associated with macroaggregates is more readily mineralized than that associated with microaggregates. Tisdall and Oades [11], Elliot [126], and others [127] suggested that aggregation is an important factor in controlling organic matter levels and the nutrient flow in soil. Therefore, availability of organic materials as substrates for microorganisms is not determined only by chemical constitution, but also by their location in soil. This view has also been supported by Tiessen and Stewart [128], who demonstrated that organic matter associated with the fine clay (<0.2 μm) of a soil became more rapidly depleted during 60 years of continuous cultivation, whereas losses of fine silt (5 to 2 μm) and coarse clay associated organic materials were less. The proportion of residual soil organic matter

in coarse clay- and fine silt-sized fractions increased with the time of cultivation.

B. Tillage

Changes in soil structure, as the result of tillage, have a strong influence on the decomposition and mineralization of organic materials. In undisturbed plant–soil environments, soil organic matter levels are fairly constant, but tillage alters this steady state, as the result of associated physical changes in the structure, aeration, water status, and availability of C and N as nutrient sources for microorganisms and plants [3]. A variety of models have been developed in recent years, to simulate soil organic matter development and the cycling of nutrients under long-term continuous management [22,23,129–131]. Parton et al. [122] simulated the dynamics of C, N, P, and S in uncultivated and cultivated grassland soils. After 60 years of cultivation, soil organic carbon levels had been reduced by 23%. Decomposition rates for the months when tillage occurred were increased by 25, 50, and 50% for active, slow, and passive soil organic matter pools, respectively (see Fig. 1). This reduction should be paralleled by a decrease in organic C, N, P, and S levels. The addition of N, P, and S fertilizers reduced the rate of decrease in soil carbon with cultivation and suggested that an equilibrium in soil C, N, P, and S levels should be reached after 150 to 200 years of cultivation, whereas these levels in the unfertilized soil should still be declining after this time. Other examples of continuously managed plots also show similar patterns [17, 131]. However, after reaching an equilibrium, organic matter levels do not decrease any further with regular additions of crop residues in the form of straw, together with intercropping of plants used as green manure [132]. The organic matter content of soil can be slowly increased by the regular addition of farmyard manure or by the alteration in tillage practices [1,131].

C. Effects of Growing Plants

The root systems of growing plants may disturb the association of humic compounds with inorganic materials or within aggregates [133], and they may also cause a "priming" effect (additional SOM degradation resulting from added undecomposed material) that results from root deposits that can lead to changes in the microbial activity in the rhizosphere [134]. Roots can also influence the soil that they contact by the adsorption of nutrients, particularly nitrogen. The uptake of water by roots may create localized rapid drying and rewetting effects that enhance soil organic matter degradation [135,136].

The literature on the effects of growing plants on organic carbon mineralization is, however, contradictory. Several authors [137,138] suggest that mineralization of native soil or plant residue carbon proceeds faster in a planted soil than in an unplanted soil under comparable conditions. On the other hand, it has also been reported [139,140] that growing plants tend to conserve carbon from added plant residues or from native soil. For example, Martin [140] and Reid and Goss [139], in experiments with ^{14}C-labeled plant residue or soils reported that the lower rate of $^{14}CO_2$ evolution from soil as the result of cropping was partly compensated for by the uptake of labeled carbon into roots and transport into sprouts [140]. In a recent study [141], plants were grown in a soil that was either amended with ^{14}C-labeled plant residues or the soil organic matter was uniformly ^{14}C-labeled. Plant residues were either uniformly ^{14}C-labeled or specifically in the lignin portion. The experiments were conducted in a phytotron, wherein the temperature and moisture conditions were carefully controlled, and the $^{14}CO_2$ released from planted and unplanted soils was monitored throughout the growth period. Similar to the observations of Reid and Goss [139] and Martin [140], growing corn plants did not accelerate the mineralization of plant residues, but had even a retarding effect on carbon mineralization from soil organic matter. The uptake of ^{14}C-labeled compounds from decomposing plant residues by growing plants was small (1 to 2% of the mineralized carbon) and consisted mainly of degradation products of lignin and, most probably, of phenolic compounds.

The results of these experiments seem to indicate that at medium and constant soil water tensions, growing plants have little retarding effect on the mineralization of organic residues or of soil organic matter. However, if cropping practices lead to enhanced drying and rewetting cycles, in comparison with an unplanted soil, growing plants probably may have a more critical effect on carbon mineralization.

D. Microbial Biomass

Although microbial biomass accounts only for 1 to 3% of the soil organic carbon, it is important for both decomposition of plant residues and the net energy flux in soil. It is also an important mediator of the turnover of nutrients and is more labile than the bulk of the soil organic matter [23,142–144].

This section will not address the measurement of biomass by various methods [142,143]. It only attempts to highlight some of the aspects about the role of the microbial biomass in humus formation and degradation and in functioning as a unique indicator of stress situations in soil.

As pointed out by Jenkinson [143], changes in the quantity of biomass reveal changes caused by soil management, long before such changes can be detected in the total carbon or nitrogen contents. Beck [6,7] combined the quantity of microbial biomass and several of its enzymatic activities into an index and correlated this index with the humus content of soils. By this procedure, he was able to predict long-term decreases or increases in humus levels, even before they were proved to be drastically altered. Gröblinghoff et al. [145] has used this method to characterize the microbial biomass and its activities in field plots, located near Donauwörth, Germany, that have been managed continuously for 15 years [146]. The first set of parallel plots was fertilized only with farmyard manure; the second set received manure and a low dose of mineral fertilizer; a third set was fertilized with minerals at a medium dose and also received straw and green manure; and the fourth set was heavily fertilized with inorganic fertilizer only, but most of the crop residues remained in the field. As shown in Table 5, the organic matter contents were only about 10% lower in the inorganic-fertilized than in the organic-fertilized plots. However, the decreases in microbial biomass and its enzymatic activities were in the inorganic-fertilized plots much more drastic and amounted to about 35%.

Newbould [25] reviewed the various environmental and management factors that influence humus formation and degradation. Among these, similarly to what Birch [136] first observed, the effects of alternate drying and rewetting were rather drastic in accelerating C and N mineralization in soil. Sörensen [136a] observed that repeated drying and rewetting caused a 16 to 120% increase in $^{14}CO_2$ evolution from a soil incubated for 1.5 to 8 years with ^{14}C-labeled straw, cellulose, or glucose, when compared with the same soil maintained continuously under moist conditions.

From a soil incubated with ^{14}C- and ^{15}N-labeled plant material, Amato and Ladd [32] observed that the labeled biomass decreased by 15% during the first drying and rewetting cycle, compared with a continuously moist soil. Similarly, Bottner [135] reported that about 25 to 35% of the microbial biomass was destroyed after drying and then restored upon subsequent rewetting.

Jenkinson and Powlson [147] explained the effect of drying and rewetting on biomass and on the turnover of C and N by "partial sterilization" of the microbial biomass during drying and by release of nonbiomass organic matter. After the soil is remoistened, these materials become available to the surviving microflora. Van Veen [148] suggested that the enhancement of CO_2 evolution and N mineralization after rewetting of a soil arose from increased availability of organic substrates as the result of chemical and physical reactions and the death of microbial cells during drying. He used these two factors in a model to simulate the effect of drying and

Table 5 Influence of Continuous Management[a] on Contents of Soil Organic Matter and Microbial Biomass and Its Enzymatic Activities [145]

Regular fertilization	%C_t	%N_t	Biomass[b] (mgC/100g)	Arginine ammonification	Catalase[c]	Available N[d] (mgN/100g)
1. Fym[e] only 18 Mg ha^{-1} a^{-1}	1.3	0.13	51	4.6	11.4	8.5
2. Fym[e] + inorganic fert, 12 Mg + 40 kg N ha^{-1} a^{-1}	1.3	0.14	42	4.2	10.8	9.0
3. Inorganic fert. 124 kg N ha^{-1} a^{-1} + green manure	1.2	0.14	33	3.2	9.3	7.4
4. Inorganic fert. 180 kg N ha^{-1} a^{-1}	1.1	0.14	33	2.9	7.5	5.8

[a]An Inceptisol soil for 15 years under continuous cultivation.
[b]Biomass in spring before fertilization, determined by the respiration method [146].
[c]Ammonification of arginine and catalase activity according to Refs. 6, 7, 146.
[d]Available N determined according to Stanford and Smith (1976) Soil Sci. 122:71–76.
[e]Fym = farmyard manure.

rewetting on changes in both microbial biomass and soil organic matter.

Some microbes in soil are defined as "zymogenic" organisms, which can go through a rapid phase of growth and division in the presence of readily metabolizable organic substrates and, then, when the substrates have been depleted, shut down and wait for the next input of substrate. Other organisms have been characterized as "autochthonous" and are able to maintain low and relatively constant activities by using the more resistant components of soil organic matter [143,144]. However, it is not clear what kinds of organisms utilize humic compounds in the soil environment,

wherein the compounds owe their resistance not only to their chemical structure, but mainly to the protective physical and chemical effects of interactions between the soil mineral matrix and humic compounds [14]. Once the compounds are released from this matrix as the result of alterations in management or climate, they can be slowly, but steadily, degraded. From data in the literature [149–152] and from in vitro studies with pure cultures, it is probable that organisms active in the degradation of humic compounds are also degraders of lignin. Similar to lignin, humic compounds are not readily degraded unless the media are supplemented with readily available C sources and contain relatively small concentrations of available N. Furthermore, degradation of humic compounds is largely enhanced at high oxygen tensions, which also enhance the degradation of lignin (see under Sect. II.B).

Well-aerated soils always have a marked ligninolytic activity with an appropriate microflora [153], and it is possible that this microflora is also active in the degradation of humic compounds, once their intimate association with an inorganic or a structural matrix has been disturbed.

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